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# (54) Haloalkynes and their use as fungicides

(57) A method for controlling the growth of algae and algae-like micro-organisms, comprises contacting the micro-organisms with a urethane compound of the formula

$$[I-C\equiv C-(CH_2)_n-OOC-NH-]_mR$$

in which m is 1, 2 or 3; n is 1, 2 or 3; and R is an alkyl, aryl, aralkyl, alkaryl, alkenyl, cycloalkyl or cycloalkenyl compound having from 1 to 20 carbon atoms and, optionally, substituents in addition to the m urethane substituents given in the formula. Certain urethanes of the given formula are novel. The urethanes can be incorporated into coating compositions, e.g. paints.

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SPECIFICATION

**Haloalkynes and their use as fungicides**

This invention relates to haloalkynes and their use as fungicides.

Known fungicides include mercury compounds. They have limited effectiveness and toxicity shortcomings. Copper compounds have practical activity, but a disadvantage, for many applications, is that they are coloured. Tributyltin oxide has been used, but it is relatively expensive and shows unsatisfactory stability for exterior exposure.

For special applications in water towers such as cooling and holding towers, materials such as chlorine and sodium hypochlorite have been used. However, these materials are presently considered unacceptable by the U.S. Environmental Protection Agency at least, and may be environmentally hazardous.

Although various compounds have been employed for limited use in lakes, ponds and areas of stagnant water, there has not been a wide recognition of the need for algacides in coatings until recently. It has been found possible to "load" certain compositions with materials such as zinc oxide, but this causes problems in pigmented paints and coatings, has low algacidal activity and gives stability problems.

Certain carbamates have been employed as insecticides and herbicides. The insecticide Seven (carbamyl or naphthylmethyl carbamate) is known to be algacidal at between 1 and 100 ppm. However, even when tested at 100 ppm, it only reduced the population of an axenic culture of *Chlorella pyrenoidosa* by 30% (Christie, 1969, "Pesticide Microbiology").

"Zectran", a mexacarbate formulation, has been claimed to prevent photosynthesis in blue-green algae (bacteria). However, in "normal" spray applications it did not pose a threat to aquatic algae (Snyder and Sharidan, 1974).

Phenylcarbamates, frequently employed as herbicides, have demonstrated activity against blue-green algae (bacteria). Propham, Chloropropham and Barban have caused a 50% reduction in the growth of blue-green algae in the range between 0.3 and 70 ppm (data from Hill and Wright, 1978). Barban did not inhibit all of the algae species tested.

US-A-3,923,870 describes urethanes of 1-halogen-substituted alkynes and their fungicidal activity. US-A-4,276,211 describes the use of urethanes of 1-halogen-substituted alkynes and combinations of these compounds with epoxides to provide colour-stabilised fungicides for use in coatings.

According to the present invention, a method for controlling the growth of algae and algae-like micro-organism comprises contacting the micro-organisms with a urethane compound of the formula

$$[I-C\equiv C-(CH_2)_n-OOC-NH-]_mR$$

in which m is 1, 2 or 3; n is 1, 2 or 3; and R is an alkyl, aryl, aralkyl, alkaryl, alkenyl, cycloalkyl or cycloalkenyl compound having no more than 20 carbon atoms and, optionally, substituents in addition to the m urethane substituents given in the formula.

Novel compounds of the invention are those urethane compounds of the given formula, in which R is an aralkane or substituted aryl compound.

M and n are each integers, and may be the same or different. It is often preferred that either or both should be one. A particularly preferred compound for use in the method of the invention is 3-iodo-2-propynyl N-butylcarbamate. This compound is also known under the trade name Polyphase.

Urethane compounds used in this invention can be of considerable utility as algacides, for controlling and destroying many different species of algae and algae-like micro-organisms. They can be very stable, even when incorporated into aqueous and non-aqueous compositions. They are often deactivated and/or destroyed only by prolonged exposure to high temperatures.

The urethane compounds used in the invention can possess only low toxicity towards animals (including domestic animals), birds and other wildlife, and towards man. Consequently, their use in the algacidal compositions requires only the usual good practice and procedures in handling. Such precautions are of course well established.

Laboratory tests have indicated that the urethane compounds used in the invention can be combined with other biocides as desired. Combination can both broaden and enhance activity and extend areas of utility.

The urethane compounds used in the invention may be incorporated into protective, decorative and/or coating compositions. Such compositions may contain a wide variety of conventional components in addition to the urethane compound. Such compositions may comprise, for example, from 0.01 to 12% by weight of the urethane compound. The exact concentration to be used will often depend on the stability of the urethane compound in the compositions in which it is used, and on the nature, e.g. aqueous or non-aqueous, of the composition. Higher concentrations, e.g. up to 40% by weight, may be necessary where it is desired to control and/or destroy particular micro-organisms, e.g. in conditions of well-established growth.

For use in the invention, the urethane compounds may be employed as premixed dispersions. They may also be prepared as solutions or dispersions and thereafter added to protective compositions. For example, 3-iodo-2-propynyl N-butylcarbamate is found to be soluble in water at a level of about 15-200 ppm.

Urethanes may be used, according to the invention, in a variety of compositions requiring protection and

freedom from algal growth, including wood, mortar, many paints, coatings, corkings and fillers. Urethanes can be used against algal species found in marine, fresh water, terrestial and aerial loci. They can be used against algae found in water-cooling towers and irrigation canals.

Compositions in which the urethane compounds may be incorporated include all types of water-based latex paints including acrylic and pva latex paints, chlorinated rubber-vinyl paints, oil alkyl paints, oil-based stains, pigmented paints and protective and decorative compositions, rubber and/or asphalt-containing roof coatings, inorganic and polymeric caulkings, moulding materials, sealants, silicone compositions and liquid compositions, both aqueous and non-aqueous, adapted for painting, dipping or spraying.

It has been found that the urethane compounds used in the invention are particularly valuable for applications in, for example, irrigation ditches, canals and conduits clogged by *Batrachospermun* (red algae).

It is also possible to use these algacidal compounds for control of the so-called "red tide" problem which is generally caused by one or more algal species from the class *Dinophyceae*.

The compounds may also be used to prevent odours by controlling, limiting and/or destroying the algal population in water, such as in irrigation systems, water towers, recirculating sewage water systems and similar water-holding and transporting systems.

Algal groups which can be treated effectively by the method of this invention include algae in the divisions *Chlorophyta* (green algae), *Chrysophyta* (yellow-green algae), *Cyanophyta* (blue-green algae or bacteria), *Euglenophyta* (euglenoides), *Phaeophyta* (brown algae) and *Rhodophyta* (red algae).

The following Examples illustrate the invention, or are for the purposes of comparison.

It is well known that it is usually easier to control or prevent growth than it is to kill an already-growing algal population. It is also known to be easier to control a small rather than a large population of algal organisms. The Examples are especially intended to show the algacidal properties of the tested compounds, and compositions containing them, and particularly to show illustrative data on the effectiveness of the compositions for such species as are protected by thick capsules as well as those which grow and multiply rapidly as thick colonies, such as *Scytonema* species which have thick capsules and *Nostoc* species which grow as thick colonies.

The algae used for testing the compounds and compositions for algae control and algacidal activity were obtained from Ward's Natural Science Establishment of Rochester, N.Y., U.S.A.

*Example 1*

3-Iodo-2-propynyl N-(4-chlorophenyl) carbamate 0.2 mole 3-hydroxy-1-iodopropyne (HIP) as a 70% solution in ether, dried with anhydrous sodium sulfate, was mixed with 0.2 mole p-chlorophenyl isocyanate. A few drops of dibutyltin dilaurate were added, as catalyst. An exothermic reaction took place. The mixture was refluxed until the reaction was complete. A yield of 21 g of pale cream precipitate, approximate m.p. 95-100°C, was filtered from the clear filtrate. Partial evaporation yielded 22 g of additional precipitate, m.p. 93-95°C. % Iodine = 36.8; theoretical = 37.8%

*Example 2*

3-Iodo-2-propynyl N-(3-methylphenyl)carbamate

The procedure of Example 1 was followed, except that m-tolyl isocyanate was used instead of p-chlorophenyl isocyanate. The product was isolated from the reaction mixture after standing in a freezer overnight, after an initial filtration to remove a small amount of sediment. The yield was 37 g of pale cream crystals, melting point 93°C. % Iodene = 39.97; theoretical = 40.2%.

*Example 3*

Di(3-Iodo-2-propynyl) N,N'-toluene-2,4- and 2,6-dicarbamate

HIP was reacted with a commercial preparation of mixed isomers (80% 2,4- and 20% 2,6-isomers) of toluene diisocyanate known an Mondur TD-30, a product produced by Mobay Chemical Co.

60 g of a 72% solution of HIP in ether were mixed with 200 g methylene chloride and 0.33 cc dibutyltin dilaurate, and 19.2 g Mondur TD-30 were added slowly over a period of 50 minutes. When all reactant had been added, the mixture was heated to reflux and methylene chloride was added as required (about 250 g in all) to keep the precipitate that forms dispersed. The reaction mixture was held at reflux for 2.5 hours and allowed to stand overnight. The following morning, it was filtered to obtain 51 g of a cream-coloured powder melting at 174-177°C.

*Example 4*

Di(3-Iodo-2-propynyl) N,N'-diphenylmethane-4,4'-dicarbamate

The procedure of Example 3 was followed except that the isocyanate used was diphenylmethane-4,4'-isocyanate, obtained as Mondur M from Mobay Chemical. The reaction of 39 g HIP and 25 g Mondur M yielded 55.5 g of a cream-coloured powder, m.p. 165-168°C and iodine content 40% (theoretical = 41.4%).

*Example 5*

Di(3-iodo-2-propynyl) N,N'-toluene-2,4-dicarbamate

The procedure of Example 3 was followed except that toluene-2,4-diisocyanate (Mondur TDS, Mobay Chemical) was used. The yield was 52 g of a cream-coloured powder, approximate m.p. 181-184°C and iodine content 47% (theoretical = 47.2%).

*Example 6*

3-Iodo-2-propynyl N-(phenylmethyl)carbamate

14.6 g HIP were dissolved in 20 cc ether. 0.1 cc dibutyltin dilaurate was added 16.7 g benzyl isocyanate were added over 0.5 hour. The temperature rose to 39°C and there was precipitation. Mixing was continued for an additional 0.5 hour. The reaction mixture was filtered and washed with ether to yield 20.5 g of a cream-coloured powder, m.p. 107-110°C. This product was reslurried with ether; refiltration yielded 17.5 g of very pale cream crystals, m.p. = 112-113°C. % Iodine = 39.4; theoretical = 40.3%.

*Example 7*

Polyphase (3-iodo-2-propynyl N-butylcarbamate) was tested for algacidal activity. Erdschreiber's solution (a well-known marine salt growth medium) was combined in various amounts with various quantities of an aqueous solution containing 100 mg/l Polyphase or, in a final experiment, water, to a total of 7 ml, in screw-capped tubes. The tubes were each inoculated with 3 ml of an active culture of *Prorocentrum* (which grows well on the medium). The amounts of medium and resultant Polyphase concentrations are set out in Table 1:

TABLE 1

| Erdschreiber's solution (ml) | Polyphase concentration (mg/l) |
|---|---|
| 7.00 | 0 |
| 6.50 | 5.0 |
| 6.00 | 10.0 |
| 5.50 | 15.0 |
| 5.00 | 20.0 |
| 4.50 | 25.0 |
| 4.00 | 30.0 |
| 3.50 | 35.0 |
| 3.00 | 40.0 |
| 2.50 | 45.0 |
| 2.00 | 50.0 |
| 2.00 | 0 |

After the tubes were inoculated with *Prorocentrum*, they were incubated under cool white fluorescent light (40W) at about 20°C for 2 days. They were then examined microscopically. Viable (motile) cells were observed both in control tubes without Polyphase and in the tubes containing 5 mg of Polyphase per 1. No viable cells were observed in the tubes containing concentrations of 10 mg/l or more Polyphase.

When species of green algae were employed as the inoculum, chlorosis (the bleaching or disappearance of the green colour) could often be employed to detect the toxic level of Polyphase to the algae. Microscopic examination, chlorosis or both was employed to study these species. These techniques were repeated with other unicellular and/or microscopic algal species, the test results being shown in Table 2.

*Example 8*

Further solutions were prepared as described, in Examples 7, except that the final volume in each instance, without the inoculum, was 10 ml. The inoculum consisted of filaments of algal species such as *Spirogyra* and *Scytonema*, cut pieces of large marine algae such as *Ulva*, and marble size colonies of species such as *Nostoc*. The small amount of water adhering to the filaments, pieces and colonies was ignored. Chlorosis was employed to detect the algacidal acitivity of Polyphase.

Both fresh-water and marine species were tested as described in Example 7, the results being summarised in Table 2. It was shown that Polyphase demonstrated excellent algacidal acitivity against both groups of organisms. Marine algae are separated in Table 3. That shows that Polyphase at least could have applications in the treatment of marine algal blooms, such as "red tides".

Since Polyphase is soluble in water to the extent of about 175 ppm, and analogues of varying solubility in water are available, it was concluded that saturated solutions in water would contain sufficient biocide to control the hardiest algae.

TABLE 2

| Organism | Toxic Level of Polyphase (mg/1) |
|---|---|
| Division *Chlorophyta* (Green Algae) | 5 - 40 |
| Class *Chlorophyceae* | |
| Order *Volvocales* | 10 - 20 |
| 1. *Carteria* sp. | 10 |
| 2. *Chlamydomonas rhinhardtii* | 15 |
| 3. *Eudorina* sp. | 20 |
| 4. *Haematoccus* sp. | 10 |
| 5. *Pandorina* sp. | 20 |
| 6. *Platymonas* sp. | 10 |
| 7. *Volvox* sp | 20 |
| Order *Ulotrichales* | |
| 8. *Ulothrix* sp. | 40 |
| Order *Ulvales* | |
| 9. *Ulva* sp. | 30 |
| Order *Oedogoniales* | |
| 10. *Oedogonium* sp. | 15 |
| Order *Cladophorales* | |
| 11. *Cladophora* sp. | 25 |
| 12. *Pithophora* sp. | 25 |
| Order *Chlorococcales* | 5 - 20 |
| 13. *Ankistrodesmus* sp. | 10 |
| 14. *Chlorella pyreniodosa* | 20 |
| 15. *Hydrodictyon* sp. | 5 |
| 16. *Protosiphon* sp. | 10 |
| 17. *Scenedesmus* sp. | 5 |
| Order *Zygnematales* | *15 - 30* |
| *18. Closterium* sp. | 30 |
| 19. *Mougeotia* sp | 20 |
| 20. *Spirogyra* sp. | 15 |
| Class *Charophyceae* | |
| *Order Charales* | |
| *21. Nitella* sp. | 5 |
| Division *Chrysophyta* (Yellow-Green Algae) | 15 - 35 |
| Class *Xanthophyceae* | |
| Order *Heterotrichales* | |
| 22. *Botrydiopsis* sp. | 30 |
| 23. *Tribonema* sp. | 15 |
| Order *Heterosiphonales* | |
| *24. Botrydium* sp. | 20 |
| 25. *Vaucheria* sp. | 10 |
| Class *Chrysophyceae* | |
| Order *Chrysomonadales* | |
| 26. *Synnra* sp. | 15 |
| Class *Bacillariophyceae* | |
| Order *Pennales* | |
| 27. *Navicula* sp. | 35 |
| Division *Euglenophyta* | |
| Order *Euglenlales* | |
| 28. *Astasia* sp. | 15 |
| 29. *Euglena gracilis* (green form) | 35 |
| 30. *Phacus* sp. | 15 |
| 31. *Trachelomonas* sp. | 5 |
| Division *Pyrrophyta* (Desmokontes and Dinoflagellates) | |
| Class *Desmokontae* | |
| Order *Desmonadales* | |
| 32. *Prorocentrum* sp. | 10 |
| Class *Dinophyceae* | |
| *order Perdiniales* | |

| | |
|---|---|
| 33. *Peridinium* sp. | 15 |
| Division *Rhodophyta* (Red Algae) | |
| Subclass *Bangiodeae* | |
| 34. *Porphyridium* sp. | 15 |
| Subclass Florideae | |
| 35. *Batrachospermun* sp. | 35 |
| Uncertain Systematic Position | |
| 36. *Rhodochorton* sp. | 30 |
| Uncertain Systematic Position | |
| Class *Cryptophyceae* | |
| Order *Cryptomonodales* | |
| 37. *Chilomonas* sp. | 25 |
| Division *Cyanophyta (Cyanobacteria)* | |
| Class *Myxophyceae (Myxobacteria)* | |
| [Blue-Green Algae (Bacteria)] | 15 - 75 |
| Order *Chroococcales* | 40 - 60 |
| 38. *Anacystis* sp. | 60 |
| 39. *Gloeocapsa* sp. | 40 |
| 40. *Merismopedia* sp. | 55 |
| order *Oscillatoriales* | 15 - 75 |
| 41. *Anabaena* xp. | 35 |
| 42. *Cylindrospermum* sp. | 15 |
| 43. *Gloeotrichia* sp. | 40 |
| 44. *Lyngbya* sp. | 65 |
| 45. *Nostoc* sp. | 55 |
| 46. *Oscillatoria* sp. | 60 |
| 47. *Phormidium* sp. | 75 |
| 48. *Scytonema* sp. | 60 |
| 49. *Spirulina* sp. | 25 |
| 50. *Tolypothrix* sp. | 40 |

TABLE 3

| Organism | Toxic level of Polyphase (mg/1) |
|---|---|
| Division *Chlorophyta* (Green Algae) | |
| Order *Volvocales* | |
| 1. *Platymonas* sp. | 20 |
| Order *Ulvales* | |
| 2. *Ulva* sp | 30 |
| Division *Chrysophyta* (Yellow Green Algae) | |
| Order *Chrysomonadales* | |
| 3. *Synura* sp. | 15 |
| Division *Pyrrophyta* | |
| Order *Desmonadales* | |
| 4. *Prorocentrum* sp. | 10 |
| Division *Rhodophyta* | |
| Order *Bangiales* | |
| 5. *Posphridium* sp. | 15 |
| Uncertain Systematic Position | |
| 6. *Rhodochorton* sp. | 30 |
| Division *Cyanobacteria* | |
| 7. *Spirulina* | 25 |
| Division *Phaeophyta* (Brown Algae) | |
| 8. *Fuscus* | 65 |

Protease agar plates were prepared and seeded with a "lawn" of *Chlorella pyrenoidosa* from an axenic culture. Treated, air-dried discs, containing Polyphase, or an analogue as identified in Table 4, were placed in the centre of each plate. The dishes were incubated under a cool white fluorescent light (40W) at about 20°C until algal growth was obtained (about 6 days). The size of the zone of inhibition was measured from the edge of the disc to the edge of the algal growth. The data obtained are reported in Table 5.

TABLE 4

| Compound (see given formula) | | | Reference (Example) |
|---|---|---|---|
| m | n | R | |
| 1 | 1 | 1-butyl | A (Polyphase) |
| 1 | 2 | methyl | B |
| 1 | 1 | phenyl | C |
| 1 | 1 | ethyl | D |
| 1 | 1 | cyclopropyl | E |
| 1 | 1 | 1-hexyl | F |
| 1 | 1 | 1-octyl | G |
| 1 | 1 | 4-chlorophenyl | H (1) |
| 1 | 1 | m-tolyl | I (2) |
| 2 | 1 | 80% 2,4-tolyl<br>20% 2,6-toloy | J (3) |
| 2 | 1 | 4,4'-diphenylmethane | K (4) |
| 2 | 1 | 2,4-tolyl | L (5) |
| 1 | 1 | benzyl | M (6) |

TABLE 5

| Compound | Concentration (%) | Inhibitory Zone (mm) |
|---|---|---|
| A | 1.0 | 10 |
| A | 2.0 | 11 |
| A | 5.0 | 12 |
| A | 40.0 | 13 |
| B | 1.0 | 14 |
| C | 1.0 | 9 |
| D | 1.0 | 14 |
| E | 0.5 | 10 |
| F | 1.0 | 8 |
| G | 1.0 | 7 |
| H | 1.0 | 13 |
| | 1.0 | 9 |
| I | 1.0 | 20 |
| J | 1.0 | 6 |
| K | 1.0 | 5 |
| L | 1.0 | 5 |
| M | 1.0 | 42 |

*Example 9*

Schleicher and Schnell Analytical Paper (No. 740-E, 12 mm) discs were dipped into 1-40% acetone solutions of the compound to be tested. A 'T' pin pushed through the centre of each disc was employed to hold it during dipping and subsequent drying. The treated discs were air-dried by holding them on the 'T' pins pushed into corkboard.

*Example 10*

An oil alkyd paint was prepared from the following:

| Material | Amout (l.) |
|---|---|
| Heat-bodied linseed oil | 127 |
| Alkali-refined linseed oil | 45 |
| Beckosol P296-60 (60% dry weight) | 45 |
| Mineral Spirits | 136 |
| Cobalt drier 6% | 1.4 |
| Calcium drier 6% | 2.7 |
| Anti-skinning agent | 0.9 |
| Non-chalking titanium dioxide | 40 |
| Talc | 57 |
| Suspending agent | 1.4 |

Polyphase was added at various levels. Filter paper sheets were coated or treated with the formulations (or without Polyphase) and dried. Discs 12 mm in diameter were cut from the sheets. These discs were placed on plates containing proteose agar which had been seeded with a lawn of *Chlorella pyrenoidosa* and incubated as described in Example 9. Zones of inhibition were measured as described in Example 9. The test results are recorded in Table 6.

*Example 11*

A white alkyd oil stain was prepared from the following:

| Material | Amout (l.) |
|---|---|
| Titanium dioxide | 6.64 |
| Suspension agent | 1.36 |
| Beckosol P296-60 | 82.7 |
| Raw linseed oil | 49.78 |
| Mineral spirits | 313.0 |
| Cobalt drier 6% | 0.55 |
| Calcium drier 6% | 1.59 |
| Anti-skimming agent | 0.59 |

This was tested as described in Example 10, and inhibition zone measurements are recorded in Table 6.

*Example 12*

An acrylic latex paint was prepared from the following:

| Material | Amount (l.) |
|---|---|
| Water | 193 |
| Cellosize QP-15000 | 1.4 |
| Tamol 731 (25% dry weight) | 5.0 |
| Lecithin | 0.9 |
| Ethylene glycol | 7.3 |
| Carbitol | 5.5 |
| Defoamer-999 | 5.9 |
| Titanium dioxide | 36.8 |
| Talc | 16.4 |
| Mica | 9.5 |
| Rhoplex AC35 (46% dry weight) | 183 |

This was tested as described in Example 11, and inhibition zone measurements are recorded in Table 6.

TABLE 6

| Example | Polyphase (g/l) | Zone of Inhibition (mm) |
|---|---|---|
| 10 | 0 (control) | 4 |
| 10 | 2 | 6 |
| 10 | 4 | 10 |
| 10 | 6 | 13 |
| 11 | 0 (control) | 6 |
| 11 | 3 | 8 |
| 11 | 4 | 10 |
| 11 | 6 | 13 |
| 12 | 0 (control) | 0 |
| 12 | 6 | 4 |

It was observed that a small zone of inhibition was obtained on controls (which did not contain Polyphase). This apparent anomaly is caused by the solvents and biocides which are normally added to paints and other coatings to protect them from bacterial growth. However, after application as coatings, these toxic agents are removed by weathering, leaving the coatings unprotected. Larger zones of inhibition were observed in Polyphase-protected coatings. These results clearly demonstrate the added and prolonged protection of Polyphase use.

*Example 13*

Traycote is a protective roofing coating having the following composition:

| Material | Amout (g/l) |
|---|---|
| Ethylene glycol | 23.3 |
| Natrasol 250HR | 4.0 |
| Water | 197.8 |
| Nopco NYZ | 93.2 |
| Tamol 250 | 4.7 |
| Calcium carbamate | 93.2 |
| Titanium dioxide | 65.3 |
| Talc | 279.5 |
| Acrylic latex resin | 442.6 |
| Aqueous ammonia (26 Baume) | 1.9 |
| Troysan 174 | 2.5 |

(Troysan 174 is a volatile bactericide employed for "in-can" preservation).

Polyphase was added at levels between 0.1 and 1.0% w/v to this roof coating material. The compositions were coated onto 25 mm x 76 mm glass microscope slides, allowed to dry for 2 days, and then leached with distilled water for 3 days. The coatings were cut from the slides using a razor blade and plated onto proteose agar covered with a lawn of *Chlorella pyrenoidosa* cells. The plates were incubated under cool white fluorescent light (40W) for 2 days and examined. A green "lawn" of algal cells was observed growing to the edge of a control coating (without Polyphase). The observation included growth under the surface of the control coating (as viewed in reflected light); however, no growth whatever was observed under coating samples containing at least 0.4% Polyphase. In addition, zones of inhibition between 0.5 and 4.0 mm wide were observed around the protected coatings.

*Example 14*

A commercially-available rubberised asphalt roof coating composition was tested, which has the following composition:

| Material | % |
|---|---|
| Asphalt | 50 |
| Attagel (thickener) | 15 |
| Kraton rubber | <5 |
| Lecithin and surfactants | <1 |
| Aromatic process oil | <5 |
| High flash naphtha | 24-25 |

This coating material was combined with Troysan Polyphase Af-1 formulation. The active Polyphase content of this formulation is 40% and the remaining inert ingredients are solvents. Various mixtures contained 0.0, 0.5, 1.0, 1.5 or 2.0 % Polyphase AF-1 (0.0, 0.2, 0.4, 0.6 or 0.8 % w/w active Polyphase).

These samples were applied to glass slides with a wooden tongue depressor, and dried for 3 days. They were removed from the slides with a razor blade and placed, smooth surface down, on the surface of proteose agar plates seeded with *Chlorella pyrenoidosa*. The samples were incubated for 7 days under 40W white fluorescent light at ambient temperature (about 22°C).

*Chlorella pyrenoidosa* grew up to and under the surface of the control sample (not containing Polyphase). Its growth was inhibited and it failed to grow under the surface of samples containing Polyphase at all concentration levels. Zones of inhibition were observed at 0.6 and 0.8% active Polyphase.

*Example 15*

Solutions of Polyphase in ethanol were prepared at levels of 0.0, 0.1, 0.2, 0.4, 0.6, 0.8 and 1.0 g/100 ml. The solutions were transferred to an "Omit" air dispenser and sprayed onto the surface of proteose agar in Petri dishes. The proteose agar had previously been inoculated with *Chlorella pyrenoidosa* which would grow to produce a "lawn" of cells upon the surface. The Petri dishes were incubated under 40W cool white fluorescent light for one week at ambient temperature (about 22°C).

*Chlorella pyrenoidosa* grew covering the surface of the agar sprayed with ethanol which did not contain Polyphase. Some spotty growth occurred at the 0.1 and 0.2 g/100 ml Polyphase levels. No growth at all was observed on plates having higher levels of Polyphase.

CLAIMS

1. A method for controlling the growth of algae and algae-like micro-organisms, which comprises contacting the micro-organisms with a urethane compound of the formula

$$[I\text{-}C{\equiv}C\text{-}(CH_2)_n\text{-}OOC\text{-}NH\text{-}]_mR$$

in which m is 1, 2 or 3; n is 1, 2 or 3; and R is an alkyl, aryl, aralkyl, alkaryl, alkenyl, cycloalkyl or cycloalkenyl compound having from 1 to 20 carbon atoms and, optionally, substituents in addition to the m urethane substituents given in the formula.

2. A method according to claim 1, in which m is 1.

3. A method according to claim 1 or claim 2, in which n is 1.

4. A method according to claim 1, in which the urethane compound is 3-iodo-2-propynyl N-butylcarbamate.

5. A urethane compound of the formula defined in any of claims 1 to 3, in which R is an aralkane or substituted aryl compound.

6. 3-Iodo-2-propynyl N-(4-chlorophenyl)carbamate.

7. 3-Iodo-2-propynyl N-(3-methylphenyl)carbamate.

8. Di(3-iodo-2-propynyl) N,N'-toluene-2,4-dicarbamate.

9. Di(3-iodo-2-propynyl) N,N'-toluene-2,6-dicarbamate.

10. Di(3-iodo-2-propynyl) N,N'-diphenylmethane-4,4'-dicarbamate.

11. 3-Iodo-2-propynyl N-(phenylmethyl)carbamate.

12. A method according to claim 1, in which the urethane compound is as claimed in any of claims 5 to 11.

13. A composition adapted to coat a substrate, which comprises a urethane of the formula defined in any of claims 1 to 4 or as claimed in any of claims 5 to 11.

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